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# PATENT SPECIFICATION

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 (72) Inventors GERARD LANG and ANDREE BUGAUT



## (54) COMPOSITIONS FOR DYEING KERATINIC FIBRES AND DIAZA-MEROCYANINES FOR USE THEREIN

(71) We, L'OREAL, a French body corporate of 14 Rue Royale, Paris 8e, France, do hereby declare the invention for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:—

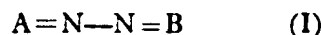
The present invention relates to compositions for dyeing keratinic fibres and diazo-merocyanines for use therein.

One of the processes which is most frequently used in hair dyeing involves the use of oxidation dyestuffs, or "bases", combined with colour modifying agents or "couplers", the latter generally being aromatic *meta*-diamines or *meta*-aminophenols, pyrazolones or diketones. In order to carry out this process, an oxidising agent such as hydrogen peroxide is added, at the time of use, to the mixture of bases and couplers chosen, which mixture has previously been rendered alkaline.

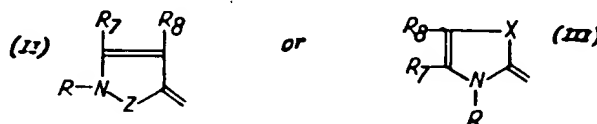
It is also known to use heterocyclic hydrazones combined with couplers to dye hair (see, for example, French Patent No. 1,599,968). However, this process has the disadvantage of requiring the use of hydrogen peroxide in an alkaline medium, and this leads to a deterioration of the hair, which rapidly becomes porous and brittle. Furthermore, the shades obtained are rather difficult to reproduce, because of the side reactions which occur in addition to the coupling reaction of the hydrazone and the coupler. To this, there is added the fact that hydrazones are compounds which tend to attack the skin, and this often leads to problems in their use.

The present invention makes it possible to avoid these disadvantages by employing, not a mixture of hydrazone and couplers, but their coupling products, which behave as direct dyestuffs which can be used at various pHs and which give rise to shades which are easy to reproduce. Accordingly, the present invention provides a composition suitable for dyeing

human hair which comprises, in solution, at least one diaza-merocyanine or diaza-merocyanine salt of the formula:

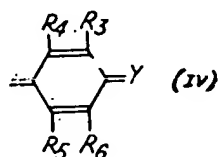


in which A represents a nitrogen-containing heterocyclic structure with 5 or 6 ring members of the formula:

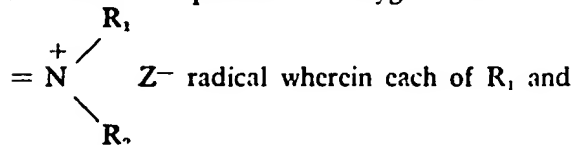


wherein R represents a lower alkyl radical (i.e. containing 1 to 4 carbon atoms) or an optionally substituted phenyl radical and X represents (i) an oxygen or sulphur atom or a NR' radical, wherein R' represents a lower alkyl radical, (ii) a —CH<sub>2</sub>— radical, optionally substituted by one or two lower alkyl radicals, or (iii) an ethylenic i.e. —CH=CH— radical or a —C=N— radical wherein R'' represents

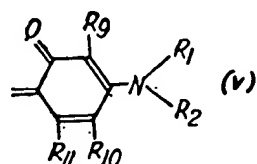
a hydrogen atom or a lower alkyl radical; Z represents an ethylenic radical or a —NR''' radical wherein R''' denotes a lower alkyl radical; R<sub>7</sub> represents a hydrogen atom, a lower alkyl radical or a phenyl radical and R<sub>8</sub> represents a hydrogen atom or a lower alkyl radical, or R<sub>7</sub> and R<sub>8</sub>, together with the carbon atoms to which they are bonded, form a condensed benzene ring which is optionally substituted by one or more halogen atoms or alkyl, alkoxy or nitro radicals; B represents a nitrogen-containing heterocyclic structure with 5 or 6 ring members, which can contain other hetero-atoms and which is one defined under A but which is not identical to A, or a ring of the formula



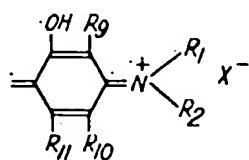
in which Y represents an oxygen atom or a



$R_1$ , which may be the same or different, represent a hydrogen atom, a lower alkyl radical or a phenyl radical and  $Z^-$  represents an organic or inorganic acid anion such as a halide, fluoborate, perchlorate, sulphate, bisulphate or acetate ion,  $R_2$  represents a hydrogen atom or a lower alkyl or lower alkoxy (i.e. containing 1 to 4 carbon atoms) radical or a phenylcarbamyl radical, each of  $R_3$  and  $R_4$ , which may be the same or different, represents a hydrogen atom or a lower alkyl or alkoxy radical and  $R_5$  represents a hydrogen atom or an amino radical which is optionally alkylated or acylated or  $R_5$  and  $R_6$ , together with the carbon atoms to which they are attached, form a condensed benzene ring; or a ring of the formula



in which either  $R_1$  and  $R_2$ , or  $R_2$  and  $R_{11}$ , form, together with the carbon and nitrogen atoms to which they are attached, a heterocyclic structure with 5 or 6 ring members, which may or may not be saturated and which can contain another hetero-atom;  $R_{11}$  being, in the first case, a hydrogen atom and  $R_2$  being a hydrogen atom or a lower alkyl radical; and  $R_{11}$  being, in the second case, a hydrogen atom and  $R_1$  being a hydrogen atom, a lower alkyl radical or an acyl radical; and  $R_{11}$  represents a hydrogen atom or a lower alkyl radical; or a ring of the formula



in which  $R_1$ ,  $R_2$ ,  $R_3$ ,  $R_{11}$ , and  $R_{11}$  are as defined above in connection with formula (V) and  $X^-$  represents an organic or inorganic anion such as halide, perchlorate, fluoborate, acetate, sulphate or bisulphate ion, it being understood that these diaza-merocyanines and

diaza-merocyanine salts can be in a mesomeric form.

The compositions according to the invention are generally aqueous or aqueous-alcoholic solutions which can easily be prepared by dissolving one or more compounds of the formula (I) in water or in a water-alcoholic mixture.

The concentration of the dyestuffs of the formula I in the dyeing compositions of this invention can vary within wide limits. The concentration is generally between only 0.001 and 0.5% by weight, because of the great affinity of these compounds for keratinic fibres.

The pH of the compositions is generally between 3 and 8. It can be adjusted to the desired value by adding an acid such as orthophosphoric acid or acetic acid or a base such as triethanolamine or ammonia.

The compositions of this invention can contain compounds of formula I as the only dyestuffs, in which case they allow shades rich in sheens which range from yellow to blue, covering the whole light spectrum, to be obtained on the hair. The compositions can, however, contain other direct dyestuffs, for example azo or anthraquinone dyestuffs, nitrobenzene dyestuffs or indoanilines, indophenols or indamines.

The compositions of this invention can also contain adjuvants usually employed in such cosmetics compositions, for example wetting agents, dispersing agents, swelling agents, penetrating agents, softeners or perfumes. They can also be packaged in aerosol flasks.

The dyeing of human hair using the compositions of this invention can be carried out in the usual manner by applying the composition to the hair, with which it is left in contact for a period varying from 3 to 30 minutes, this application being followed by rinsing, and, optionally, by washing and drying, the hair.

The present invention also provides hair wavesetting lotions which contain, in aqueous-alcoholic solution, at least one resin conventionally used in wavesetting lotions and at least one compound of formula (I). The wavesetting lotions of this invention generally contain 20 to 70% by weight of a low molecular weight alcohol, e.g. of 1 to 6 carbon atoms, in particular ethanol and isopropanol, and 1 to 3% by weight of resin.

Suitable resins which may be used in these wavesetting lotions include polyvinyl-pyrrolidone, crotonic acid-vinyl acetate copolymers, vinyl pyrrolidone-vinyl acetate copolymers and maleic anhydride-butyl vinyl ether copolymers. These resins are suitably employed in an amount from 1 to 3% by weight.

The pH of the wavesetting lotions of this invention is generally between 3 and 8. They can contain compounds of formula (I), as the only dyestuffs, in which case they form what are commonly called shading compositions.

However, they can also contain other direct dyestuffs such as those mentioned above. Furthermore, they can also contain adjuvants such as those mentioned above.

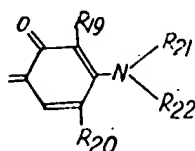
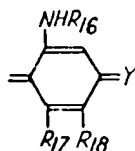
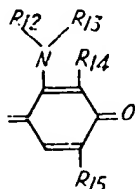
5 The wavesetting lotions according to the invention can be employed in the usual manner by applying them to the moist hair which has previously been washed and rinsed and then curling up and drying the hair.

10 The dyestuffs of formula (I) can also be employed in the form of hair lacquers, which contain at least one resin and at least one compound of the formula (I), in alcoholic solution. The alcohols used in these lacquers are preferably alcohols of low molecular weight such as ethanol or isopropanol. The cosmetic resins employed can be those mentioned above. Again, they are suitably incorporated in the composition in an amount from 1 to 3% by weight.

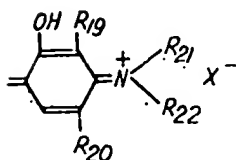
20 A certain number of the compounds of formula I are novel and thus form part of this invention. Thus the present invention also provides diazamerocyanines and salts of diazamerocyanines of the formula:



in which A is as defined above and B' is a radical corresponding to one of the formulae below:



or



in which: X<sup>-</sup> represents an organic or in-

organic anion such as a halide, fluoborate perchlorate, acetate, sulphate or bisulphate ion; R<sub>12</sub> represents a hydrogen atom or a lower alkyl radical; R<sub>13</sub> represents a hydrogen atom, a lower alkyl radical which is optionally substituted by an amino or amido radical, or a —C—R' group wherein X represents an

oxygen or sulphur atom and R' represents an amino group or a lower alkyl radical; each of R<sub>14</sub> and R<sub>15</sub>, which may be the same or different, represents a hydrogen atom or a lower alkyl radical; Y represents a =N—R<sub>1</sub>'

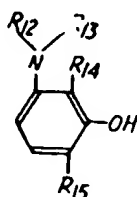
or =N<sup>+</sup> Z<sup>-</sup> radical wherein each of R<sub>1</sub>' and R<sub>2</sub>', which may be the same or different, represents a hydrogen atom or a lower alkyl radical and Z<sup>-</sup> denotes an anion of an organic or inorganic acid such as a halide, perchlorate, fluoborate, acetate, bisulphate or sulphate anion; R<sub>16</sub> represents a hydrogen atom or a —C—R' group wherein W represents an

oxygen or sulphur atom and R' represents an amino group or a lower alkyl radical; each of R<sub>17</sub> and R<sub>18</sub>, which may be the same or different, represents a hydrogen atom, a lower alkyl radical or a methoxy group, with the proviso that R<sub>18</sub> is a hydrogen atom if R<sub>1</sub>', R<sub>2</sub>' and R<sub>16</sub> are hydrogen atoms; R<sub>19</sub> and R<sub>20</sub>, together with the nitrogen and carbon atoms to which they are attached, form a saturated or unsaturated heterocyclic structure, which can contain another hetero-atom; in which case R<sub>20</sub> is a hydrogen atom and R<sub>21</sub> is a hydrogen atom or a lower alkyl radical, or R<sub>20</sub> and R<sub>21</sub>, together with the nitrogen and carbon atoms to which they are attached, form a saturated or unsaturated heterocyclic structure (generally with 5 or 6 ring members) which can contain another hetero-atom, in which case R<sub>21</sub> is a hydrogen atom and R<sub>22</sub> is a hydrogen atom, a lower alkyl radical or an acyl group; of course, these new compounds can be in a form mesomeric with that represented by formula (I').

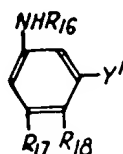
The new compounds of this invention can be obtained by condensing a hydrazone of the general formula:



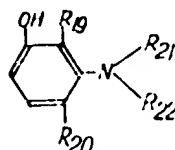
in which A is as defined above and Q represents hydrogen or a phenylsulphonyl radical with a coupler corresponding to one of the following formulae:



or



or



5

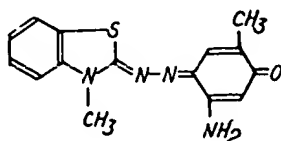
wherein Y' denotes a  $\text{—NHR}_{16}'$  or  $\text{—NH}^+ \begin{matrix} \text{R}_{17}' \\ \text{R}_{18}' \end{matrix}$

10 Z radical and the radicals  $\text{R}_{12}$  to  $\text{R}_{22}$  and  $\text{R}_{17}'$ ,  $\text{R}_{18}'$  and Z are as defined above, this condensation being carried out in the presence of an oxidising agent which may be hydrogen peroxide, an alkali metal persulphate, an alkali metal chlorite, potassium ferricyanide or ferric chloride; at a temperature of between 15 and 70° C, either in an alkaline medium, or in an acid medium in the case where it is desired to obtain a compound possessing a quaternary ammonium group. The acid employed can be that corresponding to the desired salt, or it can be a different acid, in which case the condensation is followed by an addition to the reaction medium of a salt of the acid corresponding to the salt of the desired diaza-merocyanine, the salt of the acid being more soluble in water than the said diaza-merocyanine salt; the latter is then filtered off.

25 The following Examples further illustrate the present invention. Temperatures are expressed in degrees centigrade.

#### EXAMPLE 1.

30 Preparation of 3-methyl-2,3-dihydro-benzothiazole - 2:4' - azino - 3' - amino - 6'-methyl-1'-oxo-1',4'-dihydro-benzene

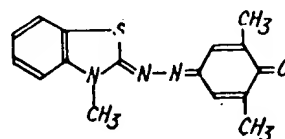


A solution of 1.60 g of 3-amino-6-methylphenol (0.01 mol) in 50 cm<sup>3</sup> of 50% strength alcohol and 5 cm<sup>3</sup> of 22° B strength ammonia are added successively to a solution of 1.80 g of 3-methyl-benzothiazolone-hydrazone (0.01 mol) in 100 cm<sup>3</sup> of 50% strength alcohol. The mixture is held at 30° C, with stirring, and then a solution of 2.28 g of ammonium persulphate in 20 cm<sup>3</sup> of 50% strength alcohol is introduced into it. Stirring is continued for 30 minutes and then the precipitate obtained is filtered off, washed with water and dried over phosphorus pentoxide.

The dyestuff is in the form of a red-brown solid with a melting point about 236°. Molecular weight found by potentiometric determination: 297 (theory: 298).

#### EXAMPLE 2.

Preparation of 3-methyl-2,3-dihydro-benzothiazole - 2:4' - amino - 2',6' - dimethyl - 1'-oxo-1',4'-dihydro-benzene

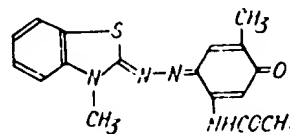


The method of operation is similar to that described in Example 1. The dyestuff is obtained in the form of a bright red solid with a melting point of 230°.

Molecular weight found by potentiometric determination: 300 (theory: 297).

#### EXAMPLE 3.

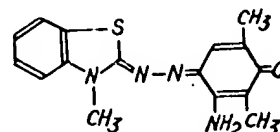
Preparation of 3-methyl-2,3-dihydro-benzothiazole - 2:4' - azino - 3' - acetamino - 6'-methyl-1'-oxo-1',4'-dihydro-benzene



The method of operation is similar to that described in Example 1. An orange-red product with a melting point above 260° is obtained. Molecular weight found by potentiometric determination: 350 (theory: 340).

#### EXAMPLE 4.

Preparation of 3-methyl-2,3-dihydro-benzothiazole - 2:4' - azino - 3' - amino - 2',6'-dimethyl-1'-oxo-1',4'-dihydro-benzene



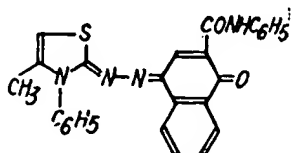
The method of operation is similar to that described in Example 1. A brown product with a melting point of 250° is obtained.

5 Molecular weight found by potentiometric determination: 321 (theory: 312).

#### EXAMPLE 5.

Preparation of 3-phenyl-4-methyl-2,3-dihydrothiazole - 2:4' - azino - 1',4' - dihydro - 1'-oxo-2'-naphthanilide

10



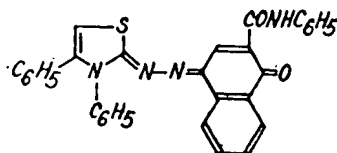
The method of operation is similar to that described in S. Hünig in "Liebigs Annalen der Chemie", volume 647, page 77.

15 A red product with a melting point of 238° is obtained.

#### EXAMPLE 6.

Preparation of 3,4-diphenyl-2,3-dihydrothiazole - 2:4' - azino - 1',4' - dihydro - 1'-oxo-2'-naphthanilide

20

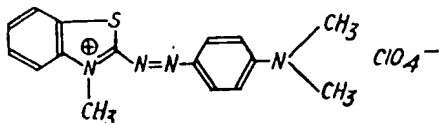


The method of operation is similar to that of Example 5.

A red product with a melting point of 240° is obtained.

25 Example 7.

Preparation of 2-[(1-dimethylamino-phenyl-(4)) - azo] - 3 - methyl - benzothiazolium perchlorate

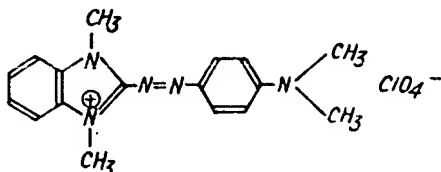


30 The method of operation is similar to that described by S. Hünig in "Liebigs Annalen der Chemie", volume 628, page 88.

A product with a green sheen and a melting point of 230° is obtained.

35 EXAMPLE 8.

Preparation of 1,3-dimethyl-2-[(1-dimethylamino-phenyl-(4)) - azo] - imidazolium perchlorate

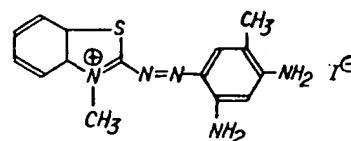


The method of operation is similar to that described by S. Hünig in "Liebigs Annalen der Chemie", volume 628, page 90.

A product with a green sheen and a melting point of 242° is obtained.

#### EXAMPLE 9.

Preparation of 2-[(1,3-diamino-6-methyl-phenyl-(4)) - azo] - 3 - methyl - benzothiazolium iodide

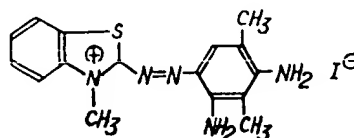


1.80 g of N-methyl-benzothiazolone, hydrazine are dissolved in 160 cm<sup>3</sup> of normal hydrochloric acid containing 10 mg of ferrous sulphate. 1.22 g of *meta*-toluylene-diamine are added, followed by 2.5 cm<sup>3</sup> of 30% strength hydrogen peroxide added with stirring. The mixture is stirred for half an hour at 30° C and then 10 cm<sup>3</sup> of formic acid are added. The mixture is heated to 70° C and filtered. 2.2 g of potassium iodide are added to the filtrate. The mixture is left to cool and the precipitate is filtered off, washed with water and dried over phosphorus pentoxide.

The dyestuff is obtained in the form of a violet-red solid with a melting point of 180° (decomposition).

#### EXAMPLE 10.

Preparation of 2-[(1,3-diamino-2,6-dimethyl-phenyl-(4)) - azo] - 3 - methyl - benzothiazolium iodide

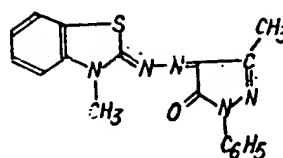


The method of operation is similar to that described in Example 9.

The dyestuff is isolated in the form of a red-violet solid with a melting point of 170° (decomposition).

#### EXAMPLE 11.

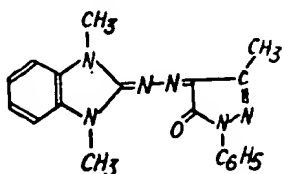
Preparation of 3-methyl-2,3-dihydro-benzothiazole - 2:4' - azino - 1' - phenyl - 3'-methyl-4'-ylidene-5'-pyrazolone



1.80 g of N-methyl-benzothiazolone-hydrazone are dissolved in 200 cm<sup>3</sup> of 50% strength methanol. A solution of 1.74 g of 1-phenyl-3-methyl-5-pyrazolone in 50 cm<sup>3</sup> of 50% strength methanol is added and then a solution of 14.5 g of potassium ferricyanide in a mixture of 100 cm<sup>3</sup> of 50% strength methanol and 10 cm<sup>3</sup> of 25% strength ammonia is introduced whilst stirring. The mixture is stirred for half an hour and then 300 cm<sup>3</sup> of water are added. The precipitate is filtered off, washed with water and dried over phosphorus pentoxide. The dyestuff is obtained in the form of an orange-red solid with a melting point of 262°.

#### EXAMPLE 12.

Preparation of 1,3-dimethyl-2,3-dihydro-benzimidazole-2:4'-azino-1'-phenyl-3'-methyl-4'-ylidene-5'-pyrazolone

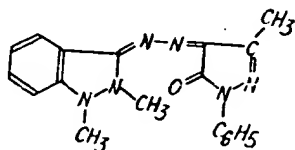


The method of operation is identical to that described in Example 11.

The dyestuff is isolated in the form of an orange-red product with a melting point of 268°.

#### EXAMPLE 13.

Preparation of 1,2-dimethyl-2,3-dihydro-indazole-3:4'-azino-1'-phenyl-3'-methyl-4'-ylidene-5'-pyrazolone



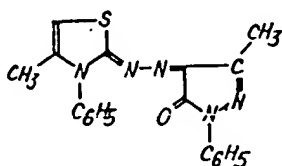
The method of operation is similar to that described in Example 11.

The dyestuff is obtained in the form of an orange-brown product with a melting point of 264°.

Molecular weight found by potentiometric determination: 348 (theory: 346).

#### EXAMPLE 14.

Preparation of 4-methyl-3-phenyl-2,3-dihydro-thiazole-2:4'-azino-1'-phenyl-3'-methyl-4'-ylidene-5'-pyrazolone

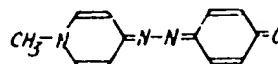


The method of operation is similar to that

described in Example 11. An orange product with a melting point of 232° is obtained.

#### EXAMPLE 15.

Preparation of 1-methyl-1,4-dihydro-pyridine-4:4'-azino-1',4'-dihydro-1'-oxo-benzene

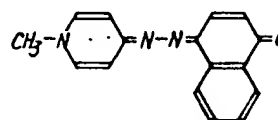


The method of operation is similar to that described by S. Hünig in "Liebigs Annalen der Chemie", volume 636, page 27.

The dyestuff is obtained in the form of a dark violet solid with a melting point of 213°.

#### EXAMPLE 16.

Preparation of 1-methyl-1,4-dihydro-pyridine-4:4'-azino-1',4'-dihydro-1'-oxo-naphthalene

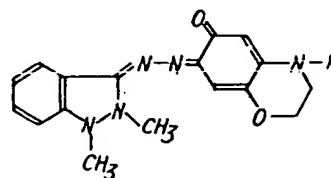


The method of operation is similar to that described by S. Hünig in "Liebigs Annalen der Chemie", volume 636, page 28.

The dyestuff is obtained in the form of a solid with a green sheen and a melting point of 225°.

#### EXAMPLE 17.

Preparation of 1,2-dimethyl-2,3-dihydro-indazole-3:7'-azino-6'-oxo-6',7'-dihydro-benzomorpholine

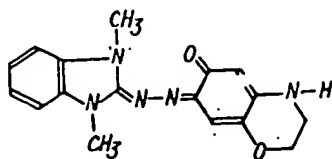


2.12 g of 1,2-dimethyl-3-indazolone-hydrazone hydrochloride are dissolved in 80 cm<sup>3</sup> of water. A solution of 1.51 g of 6-hydroxy-benzomorpholine in 80 cm<sup>3</sup> of water is added at ordinary temperature, and then a solution of 4.56 g of ammonium persulphate and 12 cm<sup>3</sup> of 22° B strength ammonia is introduced, over a period of 15 minutes, with stirring. Stirring is continued for 30 minutes and then the precipitate obtained is filtered off, washed with cold water and dried over phosphorus pentoxide. The product obtained is a brown-red dyestuff with a melting point of 230°.

#### EXAMPLE 18.

Preparation of 1,3-dimethyl-1,2-dihydro-benzimidazole-2:7'-azino-6'-oxo-6',7'-dihydro-benzomorpholine





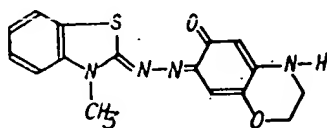
The method of operation is similar to that described in Example 17. The dyestuff is obtained in the form of a brown solid with a green sheen and a melting point of 184°.

Molecular weight found: 324

Theoretical molecular weight: 323.

#### EXAMPLE 19.

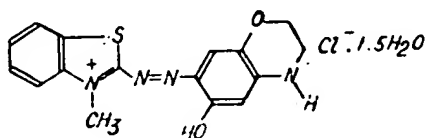
Preparation of 3-methyl-2,3-dihydro-benzothiazole-2-ylidene-azo-6'-hydroxy-benzomorpholine



The method of operation is similar to that described in Example 17. The dyestuff is obtained in the form of a brown solid with a melting point of 195°.

#### EXAMPLE 20.

Preparation of 7'-(6'-hydroxy-benzomorpholine)-2-azo-3-methyl-benzothiazolium chloride



2.52 g (0.01 mol) of N-methyl-benzothiazolone-hydrazone dihydrochloride and 1.51 g (0.01 mol) of 6-hydroxy-benzomorpholine are dissolved in 200 cc of 1N HCl, and then 26 cc of a 28% strength FeCl<sub>3</sub> solution dissolved in 24 cc of water are added over a period of 45 minutes. The mixture assumes a violet shade and a precipitate appears. The mixture is left to react for 15 minutes and then the precipitate is filtered off and dried in vacuo over phosphorus pentoxide. The chloride obtained in this way is purified by dissolving it in dimethylformamide and reprecipitating it with water. Melting point: 225° C (decomposition).

Analysis: C% 48.66—48.66 (theory 49.3)  
H% 3.87—3.99 (theory 4.62)  
N% 14.35—14.51 (theory 14.12)

#### EXAMPLE 21.

Preparation of 7'-(6'-hydroxy-benzomorpholine)-azo-3-methyl-benzothiazolium perchlorate.

This compound is obtained by dissolving the chloride prepared in Example 20 in acetic

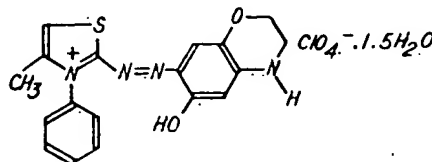
acid and reprecipitating it by means of sodium perchlorate.

Analysis: C% 42.69—42.46 (theory 42.40)  
H% 3.62—3.68 (theory 3.97)  
N% 12.43—12.55 (theory 12.37)

Melting point = 240° C (decomposition).

#### EXAMPLE 22.

Preparation of 7'-(6'-hydroxy-benzomorpholine)-azo-4-methyl-3-phenyl-thiazolium perchlorate



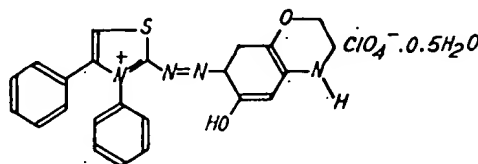
3.45 g (0.01 mol) of 4-methyl-3-phenyl-thiazolone-benzene-sulphonylhydrazone and 1.51 g (0.01 mol) of 6-hydroxy-benzomorpholine are dissolved in 100 cc of glacial acetic acid, and then 2.28 g (0.01 mol) of ammonium persulphate in 10 cc of water are added over a period of about 15 minutes. The solution assumes a violet shade. The mixture is stirred for 30 minutes and then 5 g of sodium perchlorate dissolved in 20 cc of water are added. The mixture is stirred for 1 hour and then the precipitate is filtered off and dried in vacuo over phosphorus pentoxide.

The product is purified by dissolving it in dichloroethane, filtering off the insoluble material and reprecipitating it from carbon tetrachloride. A powder with a green sheen and a melting point of 230° C is obtained in this way.

Analysis: C% 45.18—44.70 (theory 45.04)  
H% 4.07—3.94 (theory 4.17)  
N% 11.69—11.84 (theory 11.68)

#### EXAMPLE 23.

Preparation of 7'-(6'-hydroxy-benzomorpholine)-2-azo-3,4-diphenyl-thiazolium perchlorate



1.33 g (0.005 mol) of 3,4-diphenyl-thiazolone hydrazone and 0.75 g (0.005 mol) of 6-hydroxy-benzomorpholine are dissolved in 50 cc of glacial acetic acid. 2.28 g (0.01 mol) of ammonium persulphate dissolved in 10 cc of water are added over a period of 30 minutes. An intense violet colouration appears. The mixture is stirred for 30 minutes and then 2 g of sodium perchlorate dissolved in 10 cc of



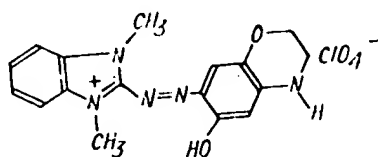
water are added. The precipitate is filtered off, washed with water and dried in vacuo over phosphorus pentoxide.

- 5 The product is purified by dissolving it in dichloroethane and precipitating it from carbon tetrachloride, thus obtaining crystals with a green sheen and a melting point of 170° C.

Analysis: C% 52.57—52.60 (theory 52.75)  
H% 4.38—4.10 (theory 3.82)  
10 N% 10.05—10.29 (theory 10.7)  
Determination of water (Karl Fisher): 1.5%.

#### EXAMPLE 24.

- Preparation of 7'-(6'-hydroxy-benzomorpholine)-2-azo-1,3-dimethyl-benzimidazolium perchlorate  
15 perchlorate



- 10 g (0.04 mol) of N,N'-dimethyl-benzimidazolone - hydrazone dihydrochloride and 6.04 g (0.04 mol) of 6-hydroxy-benzomorpholine are dissolved in 250 cc of acetic acid. 30 g of sodium acetate dissolved in 100 cc of acetic acid are added, followed by 18.24 g (0.08 mol) of ammonium persulphate dissolved in 100 cc of water added over a period of about  
25 30 minutes. The mixture is left to react for 30 minutes, and then the inorganic salts are filtered off and the product is precipitated by adding 20 g of sodium perchlorate dissolved in 300 cc of water. 9 g of product are obtained, corresponding to a yield of 70%, and the product is purified by extraction with methanol and concentration. Melting point: 240° C.

Analysis:  $C_{17}H_{14}N_4O_2 \cdot ClO_4$   
35 C% 48.6 (theory 48.2)  
H% 4.6 (theory 4.2).

#### EXAMPLE 25.

The following dyeing composition is prepared:

- 40 Vinylpyrrolidone-vinyl acetate copolymer 3 g  
Ethyl alcohol 50 cc  
Triethanolamine q.s.p. pH 5  
Dyestuff of Example 8 0.100 g  
Water, q.s.p. 100 cc

- 45 When this wavesetting lotion is applied to hair which has been dyed chestnut, it imparts a particularly aesthetic purple-chestnut shade to the head of hair.

#### EXAMPLE 26.

- 50 The following dyeing composition is prepared:

- Vinyl acetate-crotonic acid copolymer 2 g  
Ethyl alcohol 50 cc  
Benzylidene-camphor 0.2 g 55  
Triethanolamine q.s.p. pH 7  
Dyestuff of Example 7 0.1 g  
Water, q.s.p. 100 cc

When this wavesetting lotion is applied to hair which has been dyed dark blond, it imparts a very luminous ashen sheen to the head of hair.

#### EXAMPLE 27.

The following dyeing composition is prepared:

- Vinylpyrrolidone-vinyl acetate copolymer 2 g  
Ethyl alcohol 50 cc  
Hydrogen peroxide, 200 volumes strength 5 g 70  
Orthophosphoric acid, q.s.p. pH 3  
Dyestuff of Example 7 0.0012 g  
Water, q.s.p. 100 cc

This lotion is applied to naturally light chestnut hair. After the hair has been set in waves and dried, it is slightly lighter and has a particularly attractive pearly sheen.

#### EXAMPLE 28.

The following dyeing composition is prepared:

- Ethyl alcohol 50 cc  
Hydrogen peroxide, 200 volumes strength 5 g 85  
Orthophosphoric acid, q.s.p. pH 3  
Dyestuff of Example 7 0.0015 g  
Water, q.s.p. 100 cc

This lotion is applied to naturally dark blond hair. After the hair has been set in waves and dried, it is slightly lighter and has a very attractive ashen pink sheen.

#### EXAMPLE 29.

The following dyeing composition is prepared:

- Vinyl acetate-crotonic acid copolymer 2 g  
Ethyl alcohol 55 cc  
Hydrogen peroxide, 200 volumes strength 5 g 100  
Orthophosphoric acid, q.s.p. pH 3  
Dyestuff of Example 1 0.0006 g  
Dyestuff of Example 8 0.0006 g  
Water, q.s.p. 100 cc 105

This lotion is applied to naturally blond

hair. After the hair has been set in waves and dried, it is lighter and has a particularly attractive pearly ashen blond shade.

#### EXAMPLE 30.

5 The following dyeing composition is prepared:

Vinylpyrrolidone-vinyl acetate copolymer	3 g
Dyestuff of Example 4	0.03 g
10 Dyestuff of Example 1	0.1 g
96° strength alcohol, q.s.p.	100 cc

When sprayed in the form of a lacquer, this lotion gives very luminous golden sheen to a naturally blond head of hair.

#### 15 EXAMPLE 31.

The following dyeing composition is prepared:

Vinylpyrrolidone-vinyl acetate copolymer	2 g
20 Ethyl alcohol	50 cc
Triethanolamine, q.s.p. pH 7	
Dyestuff of Example 11	0.005 g
Dyestuff of Example 1	0.01 g
Dyestuff of Example 8	0.001 g
25 Water, q.s.p.	100 cc

When this lotion is applied to newly bleached hair, it imparts a silvery very light blond shade to the head of hair.

#### EXAMPLE 32.

30 The following dyeing composition is prepared:

Butylcellosolve	8 g
Propylene glycol	8 g
Alkylphenol-polyethoxyether sold under the tradename "REMCOPAL 334"	
by Messrs. GERLAND	22 g
Alkylphenol-polyethoxyether sold under the tradename "REMCOPAL 349"	
40 by Messrs. GERLAND	22 g
Ammonia, 22° B strength	8 g
Compound of Example 17	0.096 g
Water, q.s.p.	100 cc

45 20 g of hydrogen peroxide of 20 volumes strength are added to 20 g of the solution prepared in this way. A gel is obtained which, when applied to bleached hair for 10 minutes, imparts a very luminous pearly beige shade to the head of hair.

#### EXAMPLE 33.

The following dyeing composition is prepared:

Butyl "Cellosolve" (Registered Trade Mark -- ethylene glycol monobutyl ether)	8 g	55
Propylene glycol	8 g	
Alkylphenol-polyethoxyether sold under the tradename "REMCOPAL 334"		60
by Messrs. GERLAND	22 g	
Alkylphenol-polyethoxyether sold under the tradename "REMCOPAL 349"		65
by Messrs. GERLAND	22 g	
Ammonia, 22° B strength	10 g	
Compound of Example 17	0.2 g	
Water, q.s.p.	100 cc	

20 g of water are added to 20 g of the solution prepared in this way. A gel is obtained which, when applied to chestnut hair for 15 minutes, imparts a mahogany chestnut shade to the head of hair, after rinsing.

#### EXAMPLE 34.

The following dyeing composition is prepared:

Butyl "Cellosolve"	8 g	
Propylene glycol	8 g	
Alkylphenol-polyethoxyether sold under the tradename "REMCOPAL 334"		80
by Messrs. GERLAND	22 g	
Alkylphenol-polyethoxyether sold under the tradename "REMCOPAL 349"		85
by Messrs. GERLAND	22 g	
Compound of Example 8	0.050 g	
Water, q.s.p.	100 cc	

20 g of water are added to 20 g of the solution prepared in this way. A gel is obtained which, when applied for 10 minutes to previously bleached hair, imparts an iridescent blond shade to the head of hair.

#### EXAMPLE 35.

The following wavesetting lotion is prepared:

Vinylpyrrolidone-vinyl acetate copolymer	2.0 g	
Ethyl alcohol	50 cc	100
Triethanolamine, q.s.p. pH 7		
Dyestuff of Example 20	0.010 g	
Water, q.s.p.	100 cc	

50 When this lotion is applied to hair which has been dyed blond, it imparts a golden sheen with a particularly attractive effect to the head of hair.

## EXAMPLE 36.

The following dyeing composition is prepared:

5	Vinylpyrrolidone-vinyl acetate copolymer	2.0 g
	Ethyl alcohol	50 cc
	Triethanolamine, q.s.p. pH 7	
	Dyestuff of Example 22	0.012 g
	Water, q.s.p.	100 g

10 When this wavesetting lotion is applied to bleached hair, it imparts a particularly luminous golden pinkish blond shade to the head of hair.

## EXAMPLE 37.

15 The following wavesetting lotion is prepared:

	Vinylpyrrolidone-vinyl acetate copolymer	2.0 g
	Ethyl alcohol	50 cc
20	Triethanolamine, q.s.p. pH 7	
	Dyestuff of Example 24	0.01 g
	Water, q.s.p.	100 cc

25 When this lotion is applied to hair which has been dyed golden blond, it imparts a particularly luminous and attractive pearly sheen to the head of hair.

## EXAMPLE 38.

The following dyeing composition is prepared:

30	Vinylpyrrolidone-vinyl acetate copolymer	2.0 g
	Ethyl alcohol	50 cc
	Triethanolamine, q.s.p. pH 8	
	Dyestuff of Example 23	0.015 g
35	Water, q.s.p.	100 cc

When this lotion is applied to bleached hair, it imparts a pretty, very luminous light pink blond shade to the head of hair.

## EXAMPLE 39.

40 The following wavesetting lotion is prepared:

	Vinyl acetate-crotonic acid copolymer	2.0 g
	Ethyl alcohol	50 cc
45	Benzylidene-camphor	0.2 g
	Triethanolamine, q.s.p. pH 7	
	Dyestuff of Example 7	0.70 g
	Dyestuff of Example 22	0.01 g

50 When this lotion is applied to hair which has been dyed dark blond, it imparts a very luminous pearly ashen sheen to the head of hair.

## EXAMPLE 40.

The following dyeing composition is prepared:

	Vinylpyrrolidone-vinyl acetate copolymer	2.0 g
	Ethyl alcohol	50 cc
	Triethanolamine, q.s.p. pH 7	
	Dyestuff of Example 22	0.010 g
	N-[(4'-Amino-2'-methoxy-3',5'-dimethyl)-phenyl]-2,5-dimethyl-benzoquinone-imine	0.010 g
	Water, q.s.p.	100 cc

When this wavesetting lotion is applied to light blond hair, it imparts a particularly attractive pearly ashen shade to the head of hair.

## EXAMPLE 41.

The following dyeing composition is prepared:

	Ethyl alcohol	50 cc
	Dyestuff of Example 24	0.012 g
	N-[(4'-Hydroxy)-phenyl]-3-amino-6-methyl-benzoquinone-imine	0.010 g
	N-[(4'-Amino-2'-methoxy-3',5'-dimethyl)-phenyl]-2,6-dimethyl-benzoquinone-imine	0.002 g
	Water, q.s.p.	100 cc

When this composition is applied to heavily bleached hair for 20 minutes, it imparts a particularly attractive golden apricot shade to the head of hair.

## EXAMPLE 42.

The following dyeing composition is prepared:

	Vinylpyrrolidone-vinyl acetate copolymer	2.0 g
	Ethyl alcohol	50 cc
	Triethanolamine, q.s.p. pH 7	
	Dyestuff of Example 20	0.005 g
	Dyestuff of Example 24	0.005 g
	N-[(4'-Hydroxy)-phenyl]-3-amino-6-methyl-benzoquinone-imine	0.0025 g
	N-[(4'-Amino-2'-methoxy-3',5'-dimethyl)-phenyl]-2,5-dimethyl-benzoquinone-imine	0.001 g
	Water, q.s.p.	100 cc

When this wavesetting lotion is applied to blond hair, it imparts a particularly attractive pearly sheen to the head of hair.

## EXAMPLE 43.

The following wavesetting lotion is prepared:

5	Vinylpyrrolidone-vinyl acetate copolymer	2.0 g
	Ethyl alcohol	50 cc
	Triethanolamine, q.s.p. pH 7	
	Benzylidene-camphor	0.2 g
	Dyestuff of Example 24	0.006 g
10	Dyestuff of Example 22	0.004 g
	N-[(4'-Hydroxy)-phenyl]-3-amino-6-methylbenzoquinone-imine	0.001 g
15	N-[(4'-Amino-2'-methoxy-5'-methyl)-phenyl]-3-acetyl-amino-6-methylbenzoquinone-imine	0.005 g
	Water, q.s.p.	100 cc

When this lotion is applied to naturally very light blond hair, it imparts a very luminous pearly ashen sheen to the head of hair.

## EXAMPLE 44.

The following wavesetting lotion is prepared:

25	Vinylpyrrolidone-vinyl acetate copolymer	2.0 g
	Ethyl alcohol	50 cc
	Triethanolamine, q.s.p. pH 6	
	Dyestuff of Example 23	0.007 g
30	N-(4'-Amino-2'-methoxy-3',5'-dimethyl)-phenyl-2,5-dimethyl-benzoquinone-imine	0.003 g
35	N-(4'-Hydroxy)-phenyl-2,6-dimethyl-benzoquinone-imine	0.003 g
	Water, q.s.p.	100 cc

When this wavesetting lotion is applied to hair which has been dyed light blond, it imparts a very attractive pearly ashen sheen to the head of hair.

## EXAMPLE 45.

The following dyeing composition is prepared:

45	Vinylpyrrolidone-vinyl acetate copolymer	2.0 g
	Ethyl alcohol	60 cc
	Triethanolamine, q.s.p. pH 9	
	Dyestuff of Example 22	0.010 g
50	Nitro- <i>para</i> -phenylenediamine	0.010 g
	Water, q.s.p.	100 cc

When this wavesetting lotion is applied to hair which has been dyed light-chestnut, it imparts a particularly attractive golden coppery sheen to the head of hair.

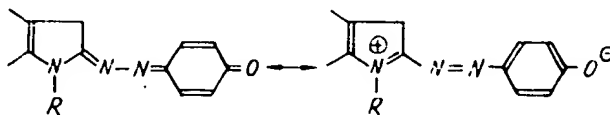
## EXAMPLE 46.

The following dyeing composition is prepared:

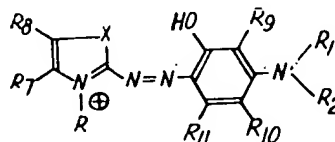
	Crotonic acid-vinyl acetate 70/30 copolymer	2.0 g	60
	Ethyl alcohol	50 cc	
	Triethanolamine, q.s.p. pH 6		
	Dyestuff of Example 22	0.010 g	
	Dyestuff of Example 23	0.010 g	
	4-Methyl-8-di- $\beta$ -hydroxyethylamino-morpholino-(2,3-b)-phenoxazonium bromide	0.010 g	65
	Water, q.s.p.	100 cc	

When this composition is applied as a wavesetting lotion to hair which has been bleached and dyed dark chestnut, it imparts a very luminous bluish ashen sheen thereto.

The dyestuff characteristics of the compounds used in this invention are believed to be due to the existence of various mesomeric forms. Thus a "neutral" form can change into an "ionic" form and vice versa. By way of example the mesomeric forms in which A is a radical of formula (III) and B is a radical of formula (IV) with Y=O can be represented by:



Again when A is a radical of formula (III) and B is a radical of formula (VI) the mesomeric form of the compound is:

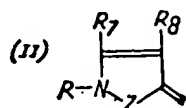


## WHAT WE CLAIM IS:—

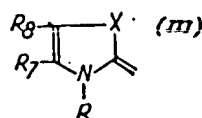
1. A composition suitable for dyeing human hair, which comprises an aqueous or aqueous-alcoholic solution, having a pH between 3 and 8, and containing 0.001 to 0.5% by weight of at least one diaza-merocyanine or salt thereof of the formula



in which A represents a nitrogen-containing heterocyclic structure with 5 or 6 ring members of the formula:

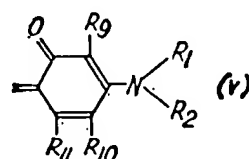


or



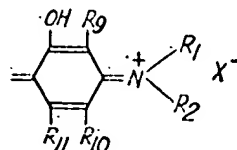
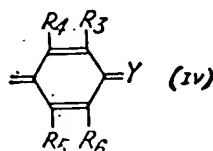
- wherein R represents a lower alkyl radical (as hereinbefore defined) or an optionally substituted phenyl radical, and X represents (i) an oxygen or sulphur atom or a NR' radical, wherein R' represents a lower alkyl radical, (ii) a  $-\text{CH}_2-$  radical optionally substituted by one or two lower alkyl radicals or (iii) an ethylenic radical or a  $-\text{C}=\text{N}-$  radical

attached, form a condensed benzene ring; or a ring of the formula

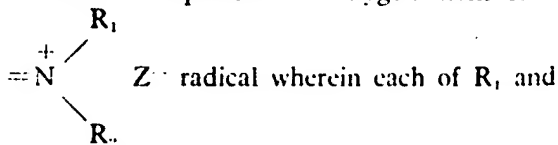


- wherein R'' denotes a hydrogen atom of a lower alkyl radical; Z represents an ethylenic radical or a NR''' radical wherein R''' denotes a lower alkyl radical; R7 represents a hydrogen atom, a lower alkyl radical or a phenyl radical, and R8 represents a hydrogen atom or a lower alkyl radical, or R7 and R8, together with the carbon atoms to which they are bonded, form a condensed benzene ring which is optionally substituted by one or more halogen atoms or alkyl, alkoxy or nitro radicals; B represents a nitrogen-containing heterocyclic structure with 5 or 6 ring members, which can contain other hetero-atoms and which may be one defined under A but which is not identical to A, or a ring of the formula

in which R1 and R2, together with the nitrogen and carbon atoms to which they are attached, form a saturated or unsaturated heterocyclic structure with 5 or 6 ring members, which can contain another hetero-atom, in which case R10 represents a hydrogen atom and R2 represents a hydrogen atom or a lower alkyl radical, or R2 and R10, together with the nitrogen and carbon atoms to which they are attached, form a saturated or unsaturated heterocyclic structure with 5 or 6 ring members, which can contain another hetero-atom, in which case R1 represents a hydrogen atom and R1 represents a hydrogen atom, a lower alkyl radical or an acyl radical and R11 represents a hydrogen atom or a lower alkyl radical, or a ring of the formula



in which Y represents an oxygen atom or a



- R2, which may be the same or different, represents a hydrogen atom, a lower alkyl radical or a phenyl radical and Z<sup>-</sup> represents an anion of an organic or inorganic acid, R1 represents a hydrogen atom or a lower alkyl or lower alkoxy (as hereinbefore defined) radical or a phenylcarbonyl radical, each of R4 and R6, which may be the same or different, represents a hydrogen atom or a lower alkyl or alkoxy radical and R5 represents a hydrogen atom or an amino radical which is optionally alkylated or acylated or R5 and R6, together with the carbon atoms to which they are

in which R1, R2, R3, R10 and R11 are as defined above and X<sup>-</sup> represents an anion of an inorganic or organic acid; or a mesomeric form thereof.

2. A composition according to Claim 1 which also contains an azo, anthraquinone or nitro-benzene dyestuff or an indoaniline, indophenol or indamine.

3. A composition according to Claim 1 or 2 in the form of a hair wavesetting lotion which contains at least one resin conventionally used in wavesetting lotions in aqueous-alcoholic solution.

4. A composition according to Claim 3 which contains from 20 to 70% by weight of low molecular weight alcohol.

5. A composition in the form of a hair lacquer which comprises, in alcoholic solution, at least one resin conventionally used in hair

lacquers and at least one diaza-merocyanine or salt thereof, as defined in Claim 1.

6. A composition according to Claim 5 which contains from 0.001 to 5.5% by weight of a diaza-merocyanine or a salt thereof.

7. A composition according to any one of Claims 3 to 6 which contains from 1 to 3% by weight of resin.

8. A composition according to any one of Claims 3 to 7 in which the resin is polyvinylpyrrolidone, a crotonic acid-vinyl acetate copolymer, a vinylpyrrolidone-vinyl acetate copolymer or a maleic anhydride-butyl vinyl ether copolymer.

9. A composition according to any one of the preceding claims which further comprises a low molecular weight alcohol.

10. A composition according to Claim 9 which comprises ethanol or isopropanol.

11. A composition according to any one of the preceding claims which also contains at least one wetting agent, dispersing agent, swelling agent, penetrating agent, softener or perfume.

12. A composition according to any one of the preceding claims which is in the form of an aerosol.

13. A composition according to any one of claims 1 to 12 in which A represents a radical of formula (III) in which X represents a sul-

phur atom or a  $-\text{NCH}_3$  radical, R represents a methyl or phenyl radical,  $R_2$  represents a methyl or phenyl radical and  $R_1$  represents a hydrogen atom, or  $R_2$  and  $R_1$ , together with the carbon atoms to which they are attached, form a condensed benzene radical.

14. A composition according to any one of claims 1 to 12 in which A represents a radical

of formula (II) in which Z represents  $-\text{NCH}_3$  radical, R represents a methyl radical and  $R_2$  and  $R_1$ , together with the carbon atoms to which they are attached, form a condensed benzene radical.

15. A composition according to any one of claims 1 to 14 in which B represents a radical of formula (IV) in which  $R_3$  represents a methyl radical, Y represents an oxygen atom

or a  $=\text{NH}_2$  or  $=\text{N}(\text{CH}_3)_2$  radical,  $R_3$  represents an amino group or an acetylamino group and  $R_4$  represents a methyl radical, or  $R_4$  and  $R_3$ , together with the adjacent carbon atoms, form a condensed benzene radical.

16. A composition according to any one of claims 1 to 14 in which B represents a radical of formula (V) in which  $R_1$  represents a hydrogen atom,  $R_{11}$  represents a hydroxyl radical, and  $R_2$  and  $R_{10}$ , together with the nitrogen and carbon atoms to which they are attached, form a

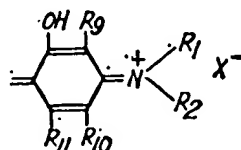


60

ring.

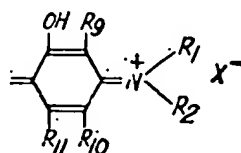
17. A composition according to any one of the preceding claims in which the diaza-merocyanine is in the form of a halide, fluoborate, perchlorate, sulphate, bisulphate or acetate.

18. A composition according to any one of claims 1 to 12 in which, if present,  $R_3$  represents a hydrogen atom or a lower alkyl or lower alkoxy radical,  $R_3$  and  $R_4$  do not form a ring with the carbon atoms to which they are attached, Z represents a halide, fluoborate, perchlorate, sulphate or acetate ion, and B does not represent a ring of the formula:



in which  $R_1$ ,  $R_2$ ,  $R_3$ ,  $R_{10}$ ,  $R_{11}$  and  $X^-$  are as defined in claim 1.

19. A composition according to any one of claims 1 to 12 in which B represents a ring of the formula:



in which  $R_1$ ,  $R_2$ ,  $R_3$ ,  $R_{10}$ ,  $R_{11}$  and  $X^-$  are as defined in claim 1.

20. A composition according to claim 1 or 5 substantially as hereinbefore described.

21. A composition according to claim 1 or 5 substantially as described in any one of Examples 25 to 46.

22. A method of dyeing human hair which comprises applying thereto a composition as claimed in any one of claims 1, 2 and 9 to 21 for between 3 and 30 minutes and then rinsing the hair and optionally washing and drying it.

23. A method of setting human hair which comprises applying to moist hair which has previously been washed and rinsed a composition as claimed in any one of claims 3, 4 and 9 to 21, curling up the hair and then drying it.

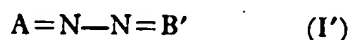
24. A method according to claim 22 or 23 in which the composition is one claimed in claim 18.

25. A method according to claim 22 or 23

in which the composition is one claimed in claim 19.

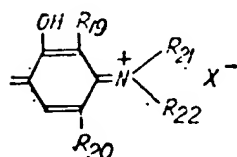
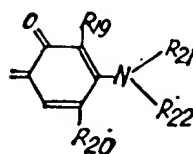
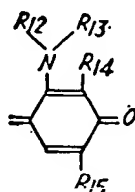
26. A method according to claim 22 or 23 substantially as hereinbefore described.

5 27. A compound of the formula:



wherein A is as defined in claim 1 and B' represents a radical corresponding to one of the formulae:

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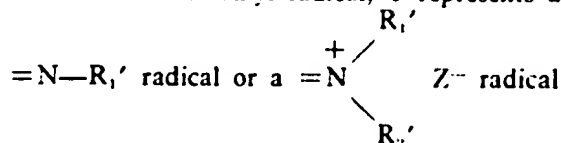


15 in which; X<sup>-</sup> represents an anion derived from an inorganic or organic acid, R<sub>12</sub> represents a hydrogen atom or a lower alkyl (as hereinbefore defined) radical, R<sub>13</sub> represents a hydrogen atom, a lower alkyl radical which is optionally substituted by an amino or amido radical, or a —C—R' group wherein X repre-

20  $\begin{array}{c} \text{X} \\ | \\ \text{C} \end{array}$ —R' group wherein X repre-

sents an oxygen or sulphur atom and R' denotes an amino group or a lower alkyl radical, each of R<sub>14</sub> and R<sub>15</sub>, which may be the same or different, represents a hydrogen atom or a lower alkyl radical, Y represents a

25 =N—R<sub>1</sub>' radical or a



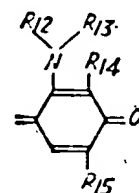
wherein each of R<sub>1</sub>' and R<sub>2</sub>', which may be the same or different, represents a hydrogen

atom or a lower alkyl radical and Z<sup>-</sup> denotes an anion of an organic or inorganic acid, R<sub>16</sub> represents a hydrogen atom or a —C—R' 30



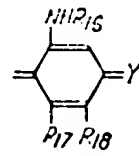
group wherein W represents an oxygen or sulphur atom and R' represents an amino group or a lower alkyl radical, each of R<sub>17</sub> and R<sub>18</sub>, which may be the same or different, represents a hydrogen atom, a lower alkyl radical or a methoxy group, with the proviso that R<sub>17</sub> is a hydrogen atom if R<sub>1</sub>', R<sub>2</sub>' and R<sub>16</sub> are hydrogen atoms, and R<sub>17</sub> and R<sub>21</sub>, together with the nitrogen and carbon atoms to which they are attached, form a saturated or unsaturated heterocyclic structure with 5 or 6 ring members, which can contain another hetero-atom, in which case R<sub>21</sub> represents a hydrogen atom and R<sub>22</sub> represents a hydrogen atom or a lower alkyl radical, or R<sub>21</sub> and R<sub>22</sub>, together with the nitrogen and carbon atoms to which they are attached, form a saturated or unsaturated heterocyclic structure, which can contain another hetero-atom, in which case R<sub>21</sub> represents a hydrogen atom and R<sub>22</sub> represents a hydrogen atom, a lower alkyl radical or an acyl group or a mesomeric form thereof. 35 40 45 50

28. A compound according to claim 27 in which B' represents a radical of the formula: 55



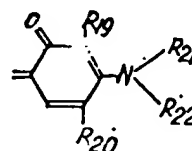
in which R<sub>12</sub>, R<sub>13</sub>, R<sub>14</sub> and R<sub>15</sub> are as defined in claim 27.

29. A compound according to claim 27 in which B' represents a radical of the formula: 60



in which R<sub>16</sub>, R<sub>17</sub>, R<sub>18</sub> and Y are as defined in claim 27 with the proviso that if Z<sup>-</sup> is present it represents a halide, perchlorate, fluoborate, acetate or sulphate ion. 65

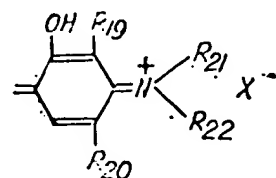
30. A compound according to claim 27 in which B' represents a radical of the formula:



in which R<sub>19</sub>, R<sub>20</sub>, R<sub>21</sub> and R<sub>22</sub> are as defined in claim 27. 70



31. A compound according to claim 27 in which B' represents a radical of the formula:



in which R<sub>19</sub>, R<sub>20</sub>, R<sub>21</sub>, R<sub>22</sub> and X are as defined in claim 27.

32. 3 - Methyl - 2,3 - dihydro - benzo-thiazole - 2:4' - azino - 3' - amino - 6'-methyl-1'-oxo-1',4'-dihydrobenzene.

33. 3 - Methyl - 2,3 - dihydro - benzo-thiazole - 2:4' - azino - 3' - acetamino - 6'-methyl-1'-oxo-1',4'-dihydrobenzene.

34. 1,3 - Dimethyl - 2 - [(1 - dimethyl-amino - phenyl - (4)) - azo - ] - imidazolium perchlorate.

35. 2-[(1,3-diamino-6-methyl-phenyl-(4))-azo]-3-methyl-benzothiazolium iodide. 15

36. 2-[(1,3-diamino-2,6-dimethyl-phenyl-(4))-azo]-3-methyl-benzothiazolium iodide.

37. 1,2 - Dimethyl - 2,3 - dihydro - indazole - 3:4' - azino - 1' - phenyl - 3' - methyl-4'-ylidene-5'-pyrazolone. 20

38. 1,2 - Dimethyl - 2,3 - dihydro - indazole - 3:7' - azino - 6' - oxo - 6',7' - dihydro-benzomorpholine.

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